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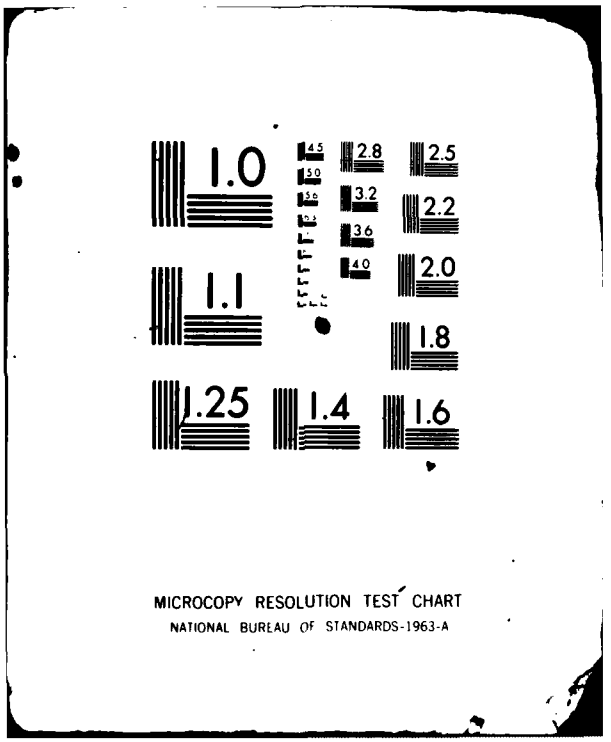
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INVESTIGATION OF LARGE DIAMETER POLYCRYSTALLINE CRUCIBLE SHAPED InP.

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Two processes are described for the synthesis of polycrystalline crucible shaped InP, vertical Bridgman and Phosphorus injection to boric oxide encapsulated Indium. While both processes appear attractive the latter is more promising since it could potentially result in in situ growth of InP.

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SUMMARY

This program was oriented towards establishing the relative merits of two processes for the growth of polycrystalline crucible shaped InP and possible exte sion of any new finding to the in-situ InP single crystal growth by the liquid encapsulation Czochralski process. The two InP synthesis processes are a) Vertical Bridgman and b) Injection of Phosphorus to B_2O_3 encapsulated Indium. It can be conclusively stated that as a result of this and other related programs, the P injection to B_2O_3 encapsulated In is a far superior process as will become evident in the discussion section to this report.

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I. INTRODUCTION

InP is becoming an important semiconductor for a wide variety of optoelectronic and microwave applications. Even though new device concepts are rapidly emerging, realization of device potentials will be limited by the defect structure of InP. The present program addressed a very important aspect of InP single crystal growth, that is the growth of polycrystalline InP in the high pressure crystal puller. Development of such a process will not only have important implications in the InP price owing to improved equipment utilization but also will have a direct effect on the quality of the material. Main emphasis during this effort was placed toward the mechanics in process development. Material characterization also received attention, specifically secondary ion mass spectrometry and van der Pawe measurements provided the basic impurity material evaluation.

II. DISCUSSION

For cost effective bulk growth of single crystal InP, synthesis of the polycrystalline charge at the InP melting point is imperative although growth from solution[1,2] has been extensively used so far. The disadvantage of the solution growth process is the small growth rate. Undoubtedly for some applications that might require extremely high purity polycrystalline InP, solution growth of InP might still be desirable.

InP synthesis at the stoichiometric point can only take place in a protective environment, i.e. an autoclave, owing to the high partial pressure of P over InP at the InP melting point(27 atm at 1062°C)[3]. Synthesis of InP, in an autoclave, by the horizontal Bridgman growth has recently been reported[4,5]. The main advantage of the growth of crucible shaped polycrystalline InP in a high pressure crystal puller relative to growth in in a horizontal Bridgman grower at high pressures is the charge shape, which has economic implications since puller capacity for single crystal growth is greatly dependent on charge shape. Another advantage is the potential, once technology is developed, for in situ growth, therefore greatly reducing machine time per unit InP single crystal. Under this program, two different processes were investigated, vertical Bridgman and P injection to B_2O_3 encapsulated In.

IIa-Vertical Bridgman

Schematically this process is shown in fig. 1. The quartz vessel is dumb bell shaped. Initially In metal is loaded to the

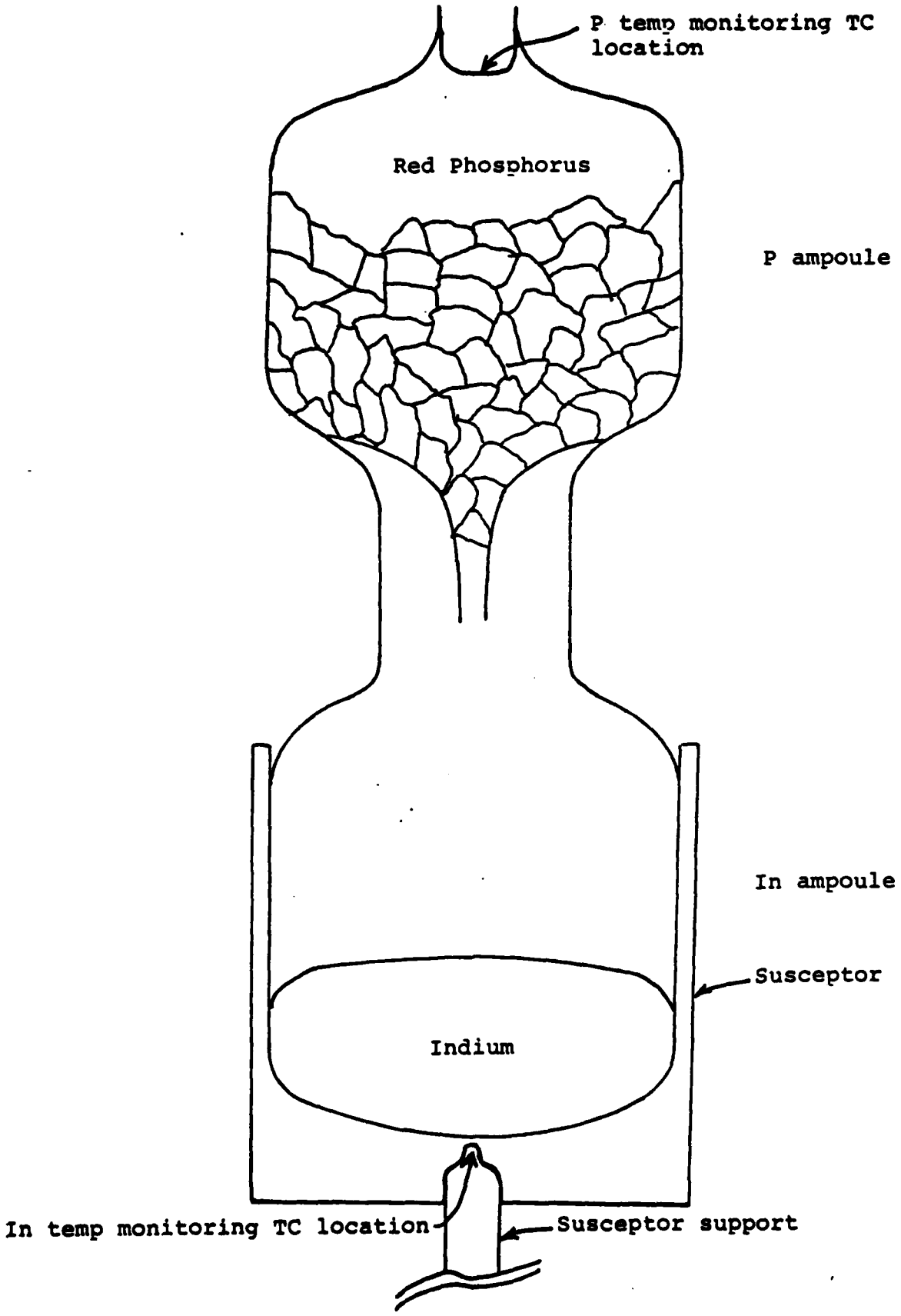

Fig. 1 Schematic representation of vertical Bridgman processes for the growth of crucible shaped polycrystalline InP.

upper compartment. Under vacuum this compartment is heated with a blow torch until In melts and flows to the bottom compartment through the funnel. Following In transfer to the lower compartment and In solidification, P is loaded to the upper compartment and the reactor tube is evacuated and sealed. Typical charge sizes are 500gm of In and 150 gm of commercial red P. The ampoule wall thickness is 2mm throughout, and the inside diameter of the In and P reservoirs is 75mm. The ampoule is loaded in the high pressure crystal puller with the In reservoir placed in the resistance heated graphite susceptor. The Phosphorus reservoir is thermally insulated with ¼" thick fiberfax insulation. This insulation reduces the severe convection cooling, and provides for a stable uniform temperature in the P reservoir. A chromel-alumel monitoring thermocouple is placed at the top of the ampoule. The In temperature is monitored with a type B (Pt-Rd 6% Pt and Pt-Rd 30% Pt) thermocouple. The reaction process typically consists of raising the In temperature to the melting point of InP, and gradually attempting to control the P pressure by monitoring the P reservoir temperature. The two parameters used for such control are the nitrogen chamber pressure, which becomes an efficient heat transport agent between the hot zone and the P reservoir, and the relative position of the ampoule in the hot zone. By trial and error procedures, we were able to adequately control this process which results in crucible shaped InP polycrystalline charges. The stoichimetry of the charges, however, varied over a rather wide range(90-98%).

It was established that the main variable in irreproducibility of the charge stoichiometry was drifting of the location of the cold spot on the P reservoir. This could be rectified by increasing the number of P temperature monitoring thermocouples which will require some minor modification in the crystal puller feedthroughs.

Fig. 2 shows a typical InP crucible shaped charge synthesized by the above process. It weighs approximately 620 gm, and has an excess In concentration of 2%. The main problem associated with the process described earlier is evident in fig. 2. The non-cylindrical shape of the charge resulted from a partial collapse of the ampoule, owing to the appreciably higher pressure of the N_2 ambient relative to the internal P pressure of the ampoule, during synthesis.

IIb-P Injection to B_2O_3 Encapsulated In

Injection of As to B_2O_3 encapsulated Ga is receiving attention for low cost high quality GaAs manufacturing. Similarly this process appears just as attractive for the growth of InP. The main attraction, of course, is the potential of in situ growth of single crystal InP. The process is schematically shown in fig. 3. Initially the encapsulated In is brought to the melting point of InP. Subsequently the P reservoir that is attached to the seed holder is lowered until the P injector is within 2mm of the bottom of the crucible. The P is indirectly heated from the hot zone and P is transported to the In containing crucible. By trial and error procedures, we were able to minimize the loss

Fig. 2 Verical Bridgman grown crucible shaped polycrystalline InP charge three inches in diameter, weighing 620gm.

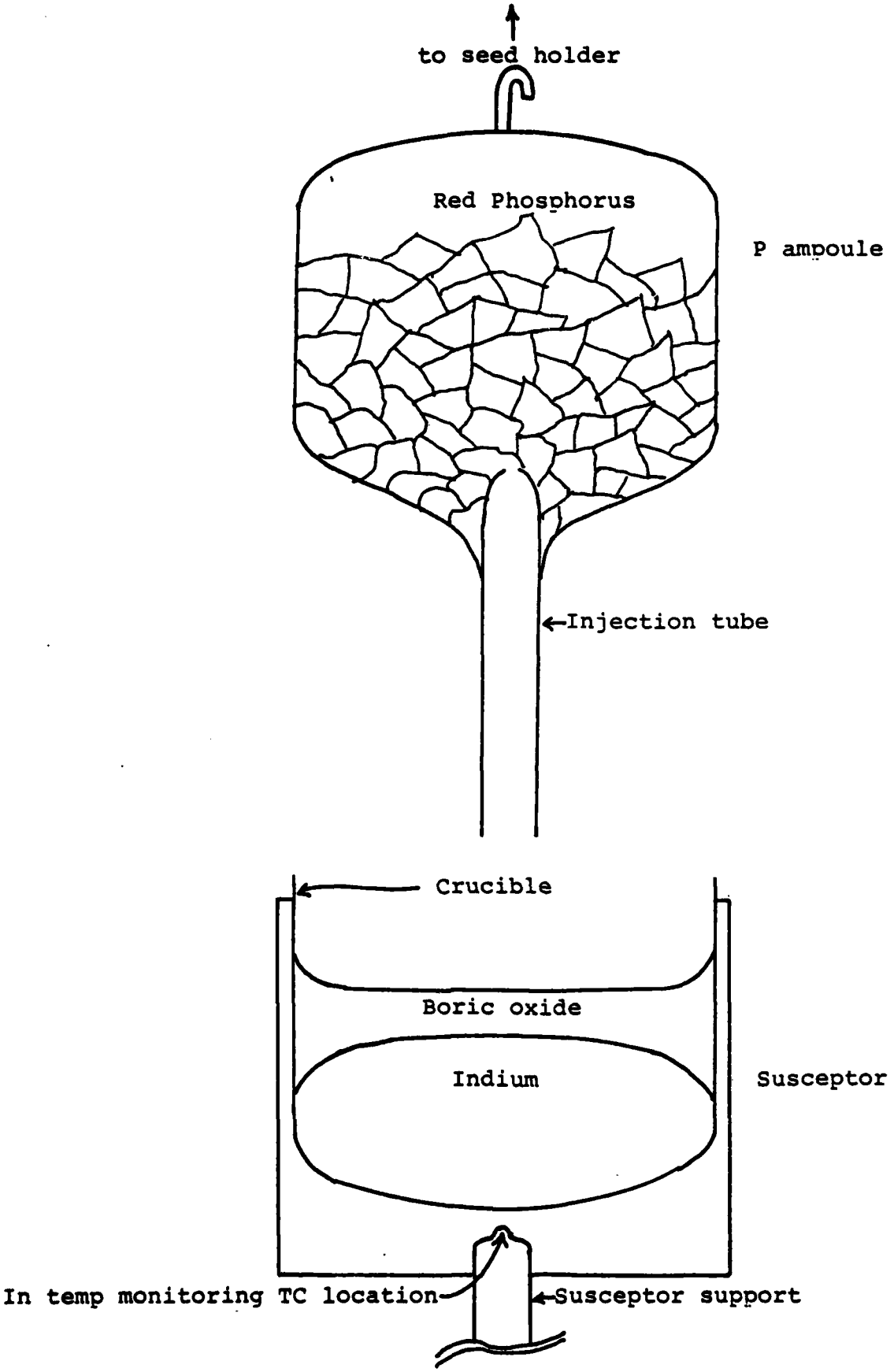

Fig. 3 Schematic representation of injection of Phosphorus to Boric Oxide encapsulated Indium.

of P during synthesis so that we can react 490 gm of In with 150 gm of P. Assuming 100 per cent reaction, the process yields 622 gm of InP with the balance of 18 gm of P accounted by the amount required to generate the P partial pressure in the ampoule and the P loss that deposists on the crystal puller walls during the reaction.

Under the above optimized conditions, this process yields nearly fully stoichiometric material. At present it is difficult to determine exactly the degree of stoichiometry because of the charge chipping associated with the B_2O_3 removal following process completion. Similarly the presence of B_2O_3 in the injector does not permit the unambiguous determination of the exact amount of P injected by measuring the crucible-charge-B_2O_3 weight after the reaction. Nevertheless our estimate of the degree of stoichiometry of the process at present is better than 99.5% and probably could very well be 100%.

III. MATERIALS CHARACTERIZATION

In addition to stoichiometric determination of the polycrystalline InP, purity is the most important parameter in establishing the viability of the polycrystalline InP synthesis process. Materials evaluation was restricted to mass spectrometry and van der Pawe measurement of the electrical properties. Table I shows the mass spectographic analysis of a polycrystalline InP charge synthesized by the injection of P to B_2O_3 encapsulated In. For comparison, the mass spectographic analysis of the In source is also shown. Basically, with the exception of Boron, all other impurities are lower or equal in concentration in the polycrystalline charge compared to their concentration in the In source. In particular, the Si concentration was lower by almost two orders of magnitude.

While measurement of the electrical properties of the polycrystalline InP were performed, the small crystallite size in some samples prevented the unambiguous determination of the mobility and carrier concentration. Therefore, for comparison purposes, we decided to grow undoped InP single crystals by LEC and evaluate the top portion of the crystal only. It is believed these measurements will provide a valid relative merit of the purity of the synthesis process. The results are outlined in table II. In short, InP single crystals grown with InP polycrystalline material prepared by vertical Bridgman had a background carrier concentration of 8×10^{15}/cc. InP single crystals, however, grown with polycrystalline InP prepared by

Table I. Mass Spectrometric Analysis (ppma)

Element	Source Indium	Polycrystalline InP
B	0.05	0.5
Na	0.3	-
Mg	0.03	0.01
Al	0.1	0.03
Si	2.0	0.03
Cl	0.1	-
Ca	0.03	0.05
Cr	0.01	-
Fe	0.05	0.01
Cu	0.1	0.02
Zn	0.02	0.02
Cd	0.02	-

Table II. ELECTRICAL PROPERTIES OF LEC GROWN INP CRYSTALS

Source Material Prepared by	$(N_D-N_A)x10^{15}/cc$		Mobility(cm^2/v-sec)	
	300°K	77°K	300°K	77°K
Vertical Bridgman	8.2	5.9	3900	12520
Phosphorus Injection				
1) Two step process	2.5	1.5	3700	10070
2) In Situ				
a) Synthesis and growth in same puller	3.8	3.3	4250	22980
b) Synthesis and growth in separate pullers	3.2	2.6	4330	20640

P injection to B_2O_3 encapsulated In had electrical properties based on the single crystal growth sequence. When the crystals were grown by the "two step process" , that is, the polycrystalline feedstock was prepared separately, followed by removal from the puller and chemical etching by the standard cleaning process prior to single crystal growth, the properties were similar to those obtained in crystals grown with polycrystalline feedstock prepared by vertical Bridgman. When the crystals, however, were grown by the "in situ process", either in the same crystal puller, or by transferrring the SiO_2 crucible with the B_2O_3 and synthesized charge to a separate but identical crystal puller*, the electrical properties of the material were noticeably better. This indicates that every effort should be made to minimize the pre-growth treatment of the reactants. Whether this is a characteristic of the CrystaComm facilities or is characteristic of the process is not known. In any event, material handling should be kept to a minimum.

*The requirement for growth in a separate crystal puller is based on occasionally large loss of Phosphorus during the synthesis. The Phosphorus typically condenses on the windows thus preventing the clear observation of the solid-liquid interface which is necessary for single crystal growth.

IV. CONCLUSIONS AND RECOMMENDATIONS

Almost from the beginning of this program, it became evident that synthesis of crucible shaped polycrystalline InP by P injection to B_2O_3 encapsulated In is far superior compared to the synthesis by vertical Bridgman, for the following reasons:

a) Reaction time---The synthesis of a 600 gm charge typically can be completed in 30 minutes, in comparison to 4-6 hours for the Bridgman grown InP. The total process time includes the heat up and cooldown cycles, normally 1 and 2 hours respectively.

b) Potential for in situ single crystal growth---This undoubtedly is of great technological importance not only for its potential effect on the cost of InP, but also on the quality of the grown single crystal since the process minimizes handling and therefore contamination.

While the basic paramenters of the injection synthesis and in situ growth of InP have been investigated, extensive effort is required for the reproducible development of these processes.

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